LASER INDUCED BREAKDOWN SPECTROSCOPY WITH PULSE WIDTH MODULATION MICROCONTROLLER-BASED THERMOELECTRIC COOLER FOR LIQUID SAMPLES

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DEDICATION

This thesis is dedicated to my beloved family (Mama, Ayah, Angah, Ude, Amal, Amjad and Wan) and to the memory of my grandfather Mohamed Taib@Ahad whom I still miss every day

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that determines elemental analysis of solid, liquid or gas sample. Although LIBS has provided excellent results in quantitative and qualitative analysis of solid samples, less attention has been given to analyse the inner portion of the liquid bulk or on its surface as liquid samples were often associated with strong splashing and shockwave. Hence, a pulse width modulation microcontroller-based thermoelectric cooler (TEC) system was proposed as a sample pre-treatment method to freeze liquid samples prior to LIBS analysis. The TEC system was built to provide a user-friendly graphical user interface (GUI) for freezing and monitoring the temperature of the sample. The construction of this system was explained. The calibration results during the freezing process and maintenance of the samples at its freezing phase demonstrated excellent performance of the developed system. The effect of incorporating the TEC system with LIBS was studied and the effectiveness and shortcomings of the TEC were highlighted. A Q-switched Nd:YAG laser (1064 nm, 6 ns and 1 Hz) and a broad spectral range spectrometer LR1 were employed for laser induced breakdown spectroscopy study. Aqueous sodium chloride (NaCl) with different concentrations, and liquids categorized with different viscosities (44.07 to 16965.80 mPa.s) and types (paste, cream, gel and oil), were utilized as studied materials. Initially, direct laser irradiation of liquid and frozen NaCl samples were analysed and later the study was focused on laser irradiation of the frozen NaCl under different temperatures (0 to -5°C). The direct irradiation on aqueous NaCl samples were carried out at concentrations ranging from 0.2 to 2.5 mol/L. The irradiation of the frozen NaCl showed a higher signal-to-noise ratio (SNR) (3x), and lower detection limit (2.5x), relative standard deviation (around 5%), maximum relative error (2% to 9%) and root mean square error of prediction (0.04 mol/L) value. The analyses of the frozen NaCl with different temperatures led to the SNR optimisation as the temperature was kept constant at the freezing point of -1°C, -2°C and -3°C for 0.2, 0.5 and 1.0 mol/L frozen samples, respectively. The next set of experiments was carried out using liquids with different viscosities and types. The analyses on sodium component of the samples by direct laser irradiation of frozen samples showed emission enhancement and higher SNR as compared to that of liquids. Frozen samples also showed smaller craters diameter and higher energy fluence. The principle component analysis (PCA) is used to compare the principle component score separation and clustering pattern between frozen and liquid samples. The frozen samples showed a more established separation and clustering as compared to those acquired from liquid samples. The spectral signal quality was also optimised when the temperature was at its freezing phase. This work showed that the TEC pre-treatment method had improved the LIBS measurement of the liquid samples by maintaining its freezing state, thereby proving its ability to be used as an alternative sample preparation method. This simple and easy-to-assemble system is also significant for real-time and in-situ analysis as it is able to simultaneously freeze the sample while monitoring its temperature.

ABSTRAK

Spektroskopi runtuh aruhan laser (LIBS) adalah teknik spektroskopi pemancaran atom yang menentukan analisis unsur bagi sampel pepejal, cecair atau gas. Walaupun LIBS telah memberikan hasil yang sangat baik dalam analisis kuantitatif dan kualitatif sampel pepejal, kurang perhatian telah diberikan untuk menganalisis bahagian dalam cecair pukal atau pada permukaannya kerana sampel cecair sering dikaitkan dengan percikan kuat dan gelombang kejut. Oleh itu, sistem penyejukan termoelektrik (TEC) berasaskan mikropengawal modulasi lebar denyut dicadangkan sebagai kaedah pra-rawatan sampel untuk membekukan sampel cecair sebelum analisis LIBS. Sistem TEC dibangunkan untuk menyediakan antara muka pengguna grafik (GUI) yang mesra pengguna bagi membeku dan memantau suhu sampel. Pembinaan sistem turut dijelaskan. Hasil penentukuran semasa proses pembekuan dan pengekalan sampel pada fasa pembekuan menunjukkan prestasi cemerlang sistem yang dibangunkan. Kesan penggabungan sistem TEC dengan LIBS telah dikaji, sementara keberkesanan dan kekurangan TEC turut ditonjolkan. Laser Q-suis Nd:YAG (1064 nm, 6 ns dan 1 Hz) dan spektrometer julat spektrum lebar LR1 digunakan untuk kajian spektroskopi runtuh aruhan laser. Natrium klorida (NaCl) akueus dengan kepekatan berbeza, dan cecair yang dikategorikan dengan kelikatan (44.07 ke 16965.80 mPa.s) dan jenis (pes, krim, gel dan minyak) berlainan digunakan sebagai bahan kajian. Pada mulanya, penyinaran terus laser bagi cecair dan bekuan NaCl telah dianalisis dan kajian seterusnya telah difokuskan pada penyinaran laser bagi bekuan NaCl pada suhu yang berbeza (0 ke -5°C). Penyinaran terus pada larutan NaCl dilakukan pada kepekatan antara 0.2 hingga 2.5 mol / L. Penyinaran bagi bekuan NaCl menunjukkan nisbah isyarat-hingar (SNR) yang lebih tinggi (3x), dan nilai rendah bagi had pengesanan (2.5x), sisihan piawai relatif (sekitar 5%), ralat relatif maksimum (2% ke 9%) dan punca min ralat kuasa dua ramalan (0.04 mol/L). Analisis NaCl beku pada suhu yang berbeza membawa kepada SNR optimum apabila suhu ditetapkan pada titik beku -1°C, -2°C dan -3°C untuk masing-masing sampel beku 0.2, 0.5 dan 1.0 mol/L. Eksperimen berikutnya dijalankan menggunakan cecair dengan kelikatan dan jenis berbeza. Analisis komponen natrium pada sampel dengan penyinaran terus laser bagi sampel beku menunjukkan peneguhan pemancaran dan SNR yang lebih tinggi berbanding dengan cecair. Sampel beku juga menunjukkan diameter kawah yang lebih kecil dan fluens tenaga yang lebih tinggi. Analisis komponen utama (PCA) digunakan untuk membandingkan pemisahan dan corak kluster bagi skor komponen utama antara sampel pepejal dengan cecair. Sampel beku menunjukkan pemisahan dan kluster yang lebih mantap berbanding dengan apa yang diperoleh daripada sampel cecair. Kualiti isyarat spektrum juga dioptimumkan apabila sampel berada dalam fasa beku. Kajian ini menunjukkan bahawa kaedah pra-rawatan TEC telah menambah baik pengukuran LIBS bagi sampel cecair dengan mengekalkannya dalam keadaan beku, lalu membuktikan keupayaannya untuk digunakan sebagai alternatif kaedah penyediaan sampel. Sistem yang ringkas dan mudah-untuk-dipasang ini juga penting untuk analisis masa-nyata dan in-situ kerana ia dapat membekukan sampel dan memantau suhunya secara serentak.

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LIST OF ABBREVIATIONS

2D	-	Two-dimensional
A	-	Ampere
AAS	-	Atomic Absorption Spectroscopy
AC	-	Alternating Current
Al	-	Aluminum
API	-	Application Program Interface
ASCII	-	American Standard Code for Information Interchange
Atm	-	Atmosphere
B	-	Boron
Ca	-	Calcium
Cd	-	Cadmium
Ce	-	Cerium
CH	-	Channel
Cl	-	Chlorine
cm	-	Centimetre
COM port	-	Communication Port
Cr	-	Chromium
Cs	-	Cesium
Cu	-	Copper
DC	-	Direct Current
eV	-	Electron Volt
Fe	-	Ferum
FOM	-	Figures-of-Merit
FPD	-	Freezing-Point Depression
G/mm	-	Grooves Per Millimetre
Gd	-	Gadolinium
GND	-	Ground
GUI	-	Graphical User Interface
H	-	Hydrogen
Hg	-	Mercury

HSSF	-	Horrible SpreadSheet Format
Hz	-	Hertz
ICP-AES	-	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	-	Inductively Coupled Plasma Mass Spectroscopy
IDE	-	Integrated Drive Electronics
K	-	Potassium
La	-	Lanthanum
Li	-	Lithium
LIBS	-	Laser Induced Breakdown Spectroscopy
LOD	-	Limit of Detection
LTE	-	Local Thermal Equilibrium
Mg	-	Magnesium
mJ	-	Millijoule
ml	-	Millilitre
mm	-	Millimetre
Mn	-	Mangenese
mol/L	-	Moles Per Litre
MOSFET	-	Metal Oxide Semiconductor Field Effect Transistor
mPa.s	-	Milli Pascal Second
MRE	-	Maximum Relative Error
ms	-	Millisecond
N	-	Nitrogen
Na	-	Sodium
NaCl	-	Sodium Chloride
Nd	-	Neodymium
Nd:YAG	-	Neodymium-Doped Yttrium Aluminium Garnet
NIST	-	National Institute of Standards and Technology
nm	-	Nanometer
ns	-	Nanosecond
O	-	Oxygen
Pb	-	Lead
PCA	-	Principle Component Analysis
POI	-	Poor Obsfuscation Interface

Pr	-	Praseodymium
PSU	-	Power Supply Unit
PWM	-	Pulse Width Modulation
RMSEP	-	Root Mean Square Error of Prediction
RSD	-	Relative Standard Deviation
RXTX	-	Receive and Transmit
Si	-	Silicone
SNR	-	Signal-to-Noise Ratio
TEC	-	Thermoelectric Cooler
Ti	-	Titanium
USB	-	Universal Serial Bus
V	-	Volt
W		Watt
XRF	-	X-Ray Fluorescence
Zn	-	Zinc
µs	-	Microsecond

LIST OF SYMBOLS

t_d	-	Delay Time
t_b	-	Length of The Window
M_{max}	-	Maximum Mass of Material
E	-	Laser Energy
S	-	Surface Reflectivity
C_p	-	Specific Heat
T_0	-	Room Temperature
T_b	-	Boiling Point
I_{min}	-	Minimum Power Density
ρ	-	Density of Sample Material
L_v	-	Latent Heat of Vaporization of Sample Material
κ	-	Thermal Diffusivity of Sample
K	-	Kelvin
Δt	-	Laser Pulse Length
$T_{electron}$	-	Temperature of electron
T_{ion}	-	Temperature of ion
T_{plasma}	-	Temperature of plasma
n_e	-	Electron Density
ΔE	-	Highest Observed Transition
$I(\lambda)$	-	Radiation Intensity Emitted From Plasma
$\alpha(\lambda)$	-	Absorption Coefficient
$\varepsilon(\lambda)$	-	Emissivity
L	-	Plasma Length
°C	-	Degree Celsius
I_{avg}	-	Current of The Peltier Element
I_p	-	Operating Current
t_p	-	Pulse Width
T	-	Period
c	-	Hundreds

d	-	Tens
u	-	Ones
σ	-	Sample Standard Deviation of The Analytical Blank/Background Estimated in The Vicinity of The Analytical Line
m	-	Calibration Slope of The Calibration Curve.
h	-	Width of The Noise
H	-	Height of The Peak
s	-	Standard Deviation of The Residuals
M	-	Mean Value of The Predicted Concentration Of The Unknown Sample
x_i	-	Predicted Concentration from The Regression
n	-	Number of The Measurements
h_i	-	Actual Concentration of The Unknown Sample
N	-	Number of Predicted Samples
i	-	Prediction/Unknown Sample
p	-	Random Variables with A Vector of *x*
$\alpha_1' x$	-	Linear Function of The Element of *x*
α_1	-	A Vector of *p*
j	-	Number of Principle Components
%	-	Percentage
R	-	Linear Regression Coefficient
ΔT_f	-	Freezing-Point Depression
T_p	-	Temperature of Solvent
T_s	-	Temperature of Solution
i_v	-	van't Hoff Factor
K_f	-	Molal Freezing Point Depression Constant or Cryoscopic Constant
b	-	Molality of Solute

CHAPTER 1

INTRODUCTION

1.1 Overview

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that has drawn increasing attention in recent decades due to its ability to provide in-situ and rapid elemental determination [1]. The LIBS technique uses a pulsed laser beam to generate the plasma from the ablated sample mass [2]. The plasma spectrum emitted by the excited species provides a spectroscopic information of the chemical species in the target sample regardless of its physical state [3]. LIBS has proved useful in various research areas due to its ability to conduct real time data measurement, analysing diverse types of sample, adapting to various experimental surrounding and assessing remote material [2-4]. Recent LIBS applications have been many and range from aiding aluminium electrolysis industry [5], monitoring corrosion behaviour in molten metal [6], analysing gold- and silver-bearing mineral [7], diagnosing of human malignancies [8] and others.

However, the LIBS technique still produces unfavourable analytical results for analysis inside the liquid bulk or on its surface compared to those provided by the solid samples [9]. Even though the other spectroscopic techniques including inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) could provide improved detection limit for the liquid sample analysis, the operational and functional cost of both ICP-MS and ICP-AES is higher, whereas the AAS method is more time consuming [10]. On the contrary, the laser based analytical method such as LIBS demonstrates simplicity, flexibility and reduction of measurement time, making it ideal for liquid samples [10].

The most common causes of poorer sensitivity of liquid samples LIBS analysis are the complex matrix effect [11], lower ablation efficiency and shorter plasma decay lifetime [12]. Although LIBS has been established as an analytical technique that require no sample preparation method, this case may restrict its potential to compete with the other spectroscopy techniques. Regardless LIBS countless contributions, especially in providing measurements for solid samples, the future applications of LIBS can be further explored with the aid of sample preparation methods. These methods could help provide better experiment repeatability and analytical performance [13] .

Thus, previous studies have shown the involvement of several experimental configurations (horizontal [14] and vertical [15-18] liquid jet system for laminar flow, and liquid to aerosol conversion [19-23]) and sample preparation methods (liquid sample in droplet form [9, 21, 24, 25] and liquid to solid matrix layer conversion [26-30]) for the purpose of solving the inherent drawbacks revolving around liquid samples. Unfortunately, some of these alternatives involved a more complex experimental configuration which is non practical for real time on site measurements and unsuitable for a limited or hazardous sample [31].

Meanwhile, liquids to solid phase conversion exploits the strengths usually linked with solid samples, thereby eliminating the problems related to liquids (splashing and shockwave) [31, 32]. The ablation of solids provides several benefits, including lower threshold of laser energy and higher sampling acquisition rate [31]. Several approaches of liquid to solid phase conversion involved converting liquid samples with various viscosities into ice [33, 34], layer [26, 27, 29, 30], pellet [35-38] and substrate (non-permeable [9, 39-42] and permeable [32, 43-49]). However, some of these approaches have a higher tendency to be time consuming and tedious, along with an increase contamination probability amid the sample preparation process [31].

Among the physical state transformation techniques, liquid to solid phase conversion by freezing is a better option as it could maintain inherent homogeneity while reducing surface splashing, thereby providing improved LIBS measurements [31, 33]. To ensure higher LIBS measurement accuracy, it is also critical to maintain the frozen sample temperature due to its influence on ablation rate and plasma intensity [31]. Since majority of the studies in previous literature preferred using liquid nitrogen for freezing purpose [33, 34, 50], difficulties in maintaining the sample temperature is unavoidable due to the influence of the ambient temperature.

In response, this present work implemented a Thermoelectric Cooler (TEC) as a new freezing method to aid the LIBS analysis of different types of liquid samples. A Pulse Width Modulation (PWM) Microcontroller-based TEC controller system equipped with a user-friendly Graphical User Interface (GUI) is created to develop a sample pre-treatment approach that is based on the Arduino platform. The TEC is a thermoelectric energy conversion device that employs the Peltier effect by delivering heat energy from one side of the device (heat source) to the other side (heat sink) [51]. It is a noiseless, environmentally friendly and lightweight device that requires no maintenance or complex water distribution pipes [52]. On the other hand, Arduino is an inexpensive open source microcontroller based on the Atmega328P microprocessor that is developed to create control devices for various projects [53]. The goal of the TEC controller system was to provide a simple and easy-to-assemble system with the ability to simultaneously maintain the sample temperature and monitoring the temperature reading acquired from a temperature sensor.

In this thesis, we have focused on proving the feasibility of using the TEC system to freeze liquid samples while maintaining its solid form at its freezing phase throughout LIBS measurement. This approach has allowed us to provide enhanced measurement accuracy and precision when the sample was frozen before LIBS analysis. This research also explained the optimum freezing temperature of the sample by investigating the relationship between the sample temperature and spectral signal quality. We conclude that these findings are important in revolutionizing the LIBS application of liquid sample analysis.

1.2 Problem Statement

In the last decade, a number of studies have indicated LIBS as a highly potential technique for multi-elemental analysis of samples with various physical states [50, 54, 55]. Even though LIBS has contributed excellent results in the qualitative and quantitative analysis of solid samples, less attention has been given on liquid samples. This is because ablation on liquid samples tend to cause surface ripples, which lead to varied laser-to-sample distance and poorer figures-of-merit (FOM) [27, 56, 57]. In response, this research could potentially provide a new alternative in overcoming these matters.

The liquid to solid conversion by freezing is one of the simplest sample preparation methods that reduce surface splashing - a phenomenon usually linked to liquid sample. For liquid samples, only a small fragment of the laser energy is available for plasma excitation as most of the energy is used for liquid vaporization and splashing, thereby forming less efficient plasma. In contrast, enhanced emission intensity of the frozen samples was influenced by a more extensive plasma excitation [58, 59].

Addressing these issues revolving around liquids LIBS analysis, to mitigate or ideally to eliminate them, will bring new attempt on developing a new sample pre-treatment method to assist LIBS analysis. We propose an alternative freezing method which is a Pulse Width Modulation Microcontroller-Based Thermoelectric Cooler. This system can potentially reduce undesired interferences in the signal and improve the precision and accuracy of LIBS measurements. Additionally, this proposed method also involved other advantages, including less complicated laser or fiber coupling arrangement, unnecessary liquid optical transparency and is more practical to use [56].

1.3 Research Objectives

The main objectives of this study are:

(a) To analyse the performance of freezing liquid samples using the PWM microcontroller-based TEC system

(b) To determine the LIBS signal and figures-of-merit of aqueous sodium chloride solutions and its frozen form.

(c) To investigate the influence of sample temperature on spectral signal quality

(d) To determine the clustering pattern of liquid samples with various viscosities using LIBS-PCA technique.

1.4 Research Scope

Due to the potential capabilities of LIBS, and problems associated with liquid samples, the present study had been taken up to construct the LIBS system integrated with a TEC controller system. This configuration was implemented for enhancing the performance of LIBS in analysing various liquid samples. The development, calibration and performance of the PWM microcontroller-based TEC system equipped with a GUI was also described.

The most important precaution when dealing with frozen sample is controlling the sample temperature to ensure LIBS measurement accuracy [60]. Since freezing using liquid nitrogen is more preferable in most LIBS experiment [33, 34], melting could happen during data acquisition as it is harder to maintain constant contact between the sample and any cooling element for a longer period of time to ensure it is continuously frozen. The sample temperature is also quite difficult to control due to heat transfer during laser-sample interaction, and from the environment [33, 34, 50].

The PWM-microcontroller based TEC system with GUI was constructed to facilitate a more effective sample pre-treatment method for liquid samples. Its performance was evaluated by comparing the LIBS analysis of both frozen and liquid samples under similar experimental conditions. Since it is critical to maintain the frozen sample temperature due to its relationship with ablation rate and plasma intensity [59], the study of sample temperature influence on spectral signal quality was also one of our basic interests.

LIBS is also associated with some other challenges, including the matrix effects, overlapped emission spectrum, lacked of proper calibration samples, and pulse-to-pulse spectral variations [61]. Since some of the spectra that belong to certain type of sample category are quite indistinguishable, we incorporated principle component analysis (PCA) with LIBS to demonstrate the comparison of the spectra clustering pattern between the liquid and solid samples. Additionally, a multivariate analysis such as the PCA is important in overcoming these challenges while also reducing the data dimensionality, developing a classification model and providing a better graphical representation of the LIBS spectra [56, 62-64].

As for the LIBS instrumentation, it utilized a Q-switched Neodymium-Doped Yttrium Aluminium Garnet (Nd:YAG) laser operated at the fundamental wavelength of 1064 nm. The optimised laser pulse energy adopted throughout the present measurements was 100 mJ with pulse duration of 6 ns and repetition rate of 1 Hz. The laser source was focused on the sample surface so that it ablated the sample and thus creating plasma. The plasma was assumed to be in the thermodynamic equilibrium. Each element in plasma emits its characteristic spectral line that was collected by the spectrometer and analysed by comparing the spectrum with the National Institute of Standards and Technology (NIST) database.

Experiment with two sets of samples were carried out. The first set of samples were prepared from 99.9% vacuum salt diluted in de-ionized water. Nine concentrations ranging from 0.2 to 2.5 mol/L were investigated. They were sorted in two categories for used as calibration and unknown samples. This step was crucial to investigate the spectral analysis and FOM of LIBS. From these samples three different concentrations (0.2, 0.5 and 1.0 mol/L) of frozen NaCl were used for LIBS analysis under different temperature ranging from -5 to 0°C. The second set of samples involved 17 liquid samples with different viscosities (44.07 to 16965.80 mPa.s) that belong in either paste, cream, gel or oil categories. These samples were chosen due to their ample contributions in pharmaceutical and cosmetic industries as they correspond to a wide range of products concerning our daily life [36]. The analyses of these samples were done using the LIBS-PCA technique. The comparison of craters diameter and energy fluence between frozen and liquid samples was investigated. The spectral signal quality analyses were also included. In essence, the purpose of these analyses was to prove the feasibility of incorporating TEC system with LIBS.

1.5 Research Significance

This study intended to introduce a new sample preparation method specifically developed for liquid samples LIBS analysis. A number of studies on freezing the samples prior to LIBS analysis were previously published [33, 34, 50]. However, to the best of our knowledge, there is none using TEC system as the cooling element in constantly freezing the sample.

Therefore, this study focused on developing and constructing an open source TEC system for LIBS application, thereby verifying the compatibility of both elements in providing optimised LIBS measurements. A user-friendly GUI was developed in order to enhance the functioning of the PWM microcontroller-based TEC system in assisting LIBS analysis. This easy-to-assemble system was also equipped with other features including simple serial communication procedure, temperature measurement accuracy, real-time temperature reading display and plot, and data storage. Equally important, by integrating LIBS technique with TEC system, the spectral signal quality, the FOM and temperature influence analyses of this research could provide some comparison and references for future research purpose. The PCA analyses were also included to further prove the feasibility of integrating the TEC controller system on LIBS analysis of liquids with various viscosities. As an extension, this simple and easy-to-assemble system can become a new alternative in freezing liquids prior LIBS analysis. Its application is not only restricted for laboratory use but also for real-time and in-situ experimental surrounding. This study also can be applied for a wide range of liquid samples from different fields such as pharmaceutical, food chemistry, biomedical, environmental and others.

1.6 Thesis Overview

This thesis investigates the potential of using an PWM microcontroller-based TEC system as a sample pre-treatment technique prior to elemental analysis of liquid samples by using LIBS. The outline of the thesis with a brief overview of each of the chapters is elaborated below.

Chapter 1 described the motivations and challenges (problem statement) on pursuing this research, along with the research objectives, scope, and significance. Then, Chapter 2 gave a background review of the fundamentals of LIBS plasma. The key parameters that describe the LIBS plasma were discussed in detail. The basic principles of LIBS, LIBS instrumentation, LIBS application and LIBS performance analysis were described. The challenges of liquids LIBS analysis and methods on solving the challenges were reported. Brief explanation on components used in developing the TEC system and liquid samples analysed by LIBS a were also discussed.

Chapter 3 explained the experimental methodologies used in developing the PWM microcontroller-based TEC system, incorporating the TEC system and LIBS experiment, sample pre-treatment procedure, and analysing the data (figures-of-merit, PCA and image analysis). Next, Chapter 4 elaborated the calibration and performance analysis of the PWM microcontroller-based TEC system, optimisation of the experimental parameters of the LIBS system, LIBS analyses of liquid and frozen NaCl samples, LIBS analyses of liquids with various viscosities and its frozen form, and LIBS analysis of frozen NaCl under different temperature.

Lastly, Chapter 5, which is the final chapter, summarized the results together with concluding remarks. The contributions of the thesis were highlighted and suggestions for future research were presented.

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1. Harun HA, Zainal R. Improvement of laser induced breakdown spectroscopy signal for sodium chloride solution. *Malaysian Journal of Fundamental and Applied Sciences*. 2018;14:429-33. **(Published, Indexed by WOS)**
2. Harun HA, Zainal R. Performance of thermoelectric cooler with smart graphical user interface for solidifying liquid sample. *Malaysian Journal of Fundamental and Applied Sciences*. 2019. **(Accepted, Indexed by WOS)**